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TITLE: MAGNETIC ANOMALY IN SUPERCONDUCTING $TmRh_4B_4$

AUTHOR(S): J. L. Smith, C. Y. Huang, J. J. Tsou,
and J. C. Ho

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Magnetic anomaly in superconducting TmRh_4B_4 *

J. L. Smith and C. Y. Huang

Los Alamos Scientific Laboratory, Los Alamos, N.M. 87545

J. J. Tsou and J. C. Ho[†]

Wichita State University, Wichita, KS 67208

ABSTRACT

We have investigated the magnetic and superconducting properties of TmRh_4B_4 (which becomes superconducting at 9.6 K) by means of ac and dc magnetic susceptibility and specific heat measurements. At 10.7 K, an ac susceptibility peak similar to those found in spin glasses has been observed. In addition, a pronounced specific heat peak has been observed at 11.4 K. The susceptibility peak is essentially unaffected by substitution of 1% Lu or Er for the Tm, but it diminishes when much larger amounts of Er are substituted. The physical origin of this anomalous peak will be discussed.

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INTRODUCTION

In the course of a series of measurements on rare earth rhodium borides [1-3] which form a class of materials that are either superconducting ferromagnetic, or both, we have discovered a magnetic anomaly above the superconducting transition in TmRh_4B_4 . This anomaly is quite clearly not the usual type of ferromagnetic transition seen in rare earth rhodium borides. As a result, we have investigated the anomaly by means of the techniques of ac and dc magnetic susceptibility, resistivity, and heat capacity. We have found some intriguing properties that we report on here.

EXPERIMENTAL

Our samples of TmRh_4B_4 were prepared by argon arc-melting and checked by x-ray diffraction. They were tested in their arc-melted state or after various lengths of annealing at 1000°C for periods up to 90 days. The ac susceptibility was measured at frequencies from 20 to 400 Hz in zero applied magnetic field. The dc susceptibility measurements were performed in a vibrating sample magnetometer. The ac resistivity was done at 35 Hz using a spark-cut sample and four spring-loaded gold electrical contacts. Finally, the heat capacity measurements were performed by adiabatic calorimetry using pulsed heating and germanium thermometry.

RESULTS AND DISCUSSIONS

The ac susceptibility of a well-annealed TmRh_4B_4 sample is shown in Fig. 1. A magnetic-type peak is seen at 10.7 K followed by the known superconducting transition at $T_c = 9.6$ K [4]. Annealing serves simply to sharpen the transitions and to increase the height of the magnetic one. These results led to dc susceptibility measurements to address the possibility of a ferromagnetic transition at 10.7 K. At high temperatures ($T > 25$ K), a Curie-Weiss behavior was seen with a moment of $7.5 \pm 0.3 \mu_B$, equal, essentially, to the free ion value of Tm^{3+} . The paramagnetic Curie-Weiss temperature, θ , in the Curie-Weiss fit was between 0 K and 0.5 K. This low θ value makes the ferromagnetic transition at the susceptibility peak, $T_M = 10.7$ K unlikely. We made both field and temperature sweeps to define the magnetic behavior at temperatures below 20 K. We could find no

evidence for a remanent magnetic moment in demagnetizing sweeps between 9.6 K and 10.7 K. Below 9.6 K the onset of superconductivity at low magnetic fields precludes seeing any remanent magnetic moment behavior in a dc susceptibility measurement. Some temperature sweeps at various constant magnetic fields are shown in Fig. 2 where the curves are consistent with the ac behavior. In Fig. 2 it can be seen that in increasing magnetic fields the slope corresponding to the ac peak is broadened and shifted to lower temperatures.

These magnetic susceptibility results raised the question of the possibility of a second phase in our samples. We tried substitutions of 1 at.% Er or Lu for the Tm in our samples with no apparent changes in the susceptibility peak at 10.7 K. However, substitutions of 15 at.% Er or more wiped out the magnetic anomaly as shown in Fig. 1. We expect that if it were a simple second phase problem, the 15 at.% Er should not have wiped out the peak since Er is similar to Tm electronically.

To pursue further the nature of the magnetic anomaly we have also made electrical resistivity and heat capacity measurements. The resistivity was completely temperature independent between 20 K and the superconducting transition (not shown), and thus, no evidence for any long-range ordering was seen in the resistivity. On the other hand, as shown in Fig. 3, the heat capacity clearly shows a well defined peak at 11.7 K. In order to interpret the data, one would normally start out by subtracting from the total heat capacity the two basic contributions associated with the lattice and the conduction electrons. Because these contributions are not readily available, we use a simpler approach and assume that these contributions are the same as those in the nonmagnetic superconductor LuRh_4B_4 [3]. The results can be summarized as follows:

- (1) A Schottky-like anomaly with a peak temperature at ~ 20 K constitutes the major part of the heat capacity. Such an anomaly is presumably due to the crystal field effects of Tm^{3+} . Similar effects have been observed in ErRh_4B_4 [3] and $\text{Gd}_x\text{Er}_{1-x}\text{Rh}_4\text{B}_4$ [2].
- (2) As shown in Fig. 3, the sample undergoes a superconducting transition at $T_c = 9.6$ K, as indicated by the (electronic) heat capacity jump, which is basically in agreement with that determined from the susceptibility measurements. The magnitude of this heat capacity jump clearly suggests that the transition is a bulk effect.
- (3) The most interesting and unexpected anomaly occurs around $T_h = 11.4$ K, which is almost 2 K above T_c . This anomaly is likely to be closely associated with the susceptibility anomaly at T_M .
- (4) Finally, there is an upturn in the heat capacity as the temperature decreases below 5 K

(see Fig. 3). This anomaly might originate from a second Schottky anomaly with a peak temperature lower than 2 K.

It is well known that Tm can have a state with mixed valences, Tm^{2+} and Tm^{3+} [5], because Tm lies nearly at the end of the rare earth series in the periodic table. For example, Tm in TmSe is known to be in a homogeneous mixed-valence state [6,7]. If the Tm in $TmRh_4B_4$ is in an inhomogeneous mixed-valence state, then some of the Tm are in the magnetic Tm^{2+} state while the majority of them are in the singlet-ground state like the Tm in the Tm-monopnictides [8]. In this case, the ac magnetic susceptibility peak at $T_M = 10.7$ K is simply the well-known susceptibility cusp in a spin glass, in analogy to the $Y_{0.98}Dy_{0.02}$ dilute alloy which has been characterized as a spin glass [9]. We would like to point out that in the case of $Y_{0.98}Dy_{0.02}$ the specific heat peak is broad and located at a temperature below the susceptibility cusp. This is quite different in the case of $TmRh_4B_4$ in which the specific heat peak is narrow and is located at a temperature above that at which the susceptibility cusp takes place. The assumption of the Tm in $TmRh_4B_4$ being in a mixed-valence state is supported by the absence of the susceptibility anomaly in $Er_{0.15}Tm_{0.85}Rh_4B_4$, because the mixed-valence states are very sensitive to alloying [5]. In contrast to Tm being in this inhomogeneous state, Tm in $TmRh_4B_4$, like TmSe [6,7], could be in a homogeneous mixed-valence state. Then long-range magnetic ordering, as predicted by Varma and Birgeneau [10], could take place giving rise to both the susceptibility and specific heat anomalies. At present our data cannot tell whether Tm is in a homogeneous or inhomogeneous state. Further experiments are needed to clarify this.

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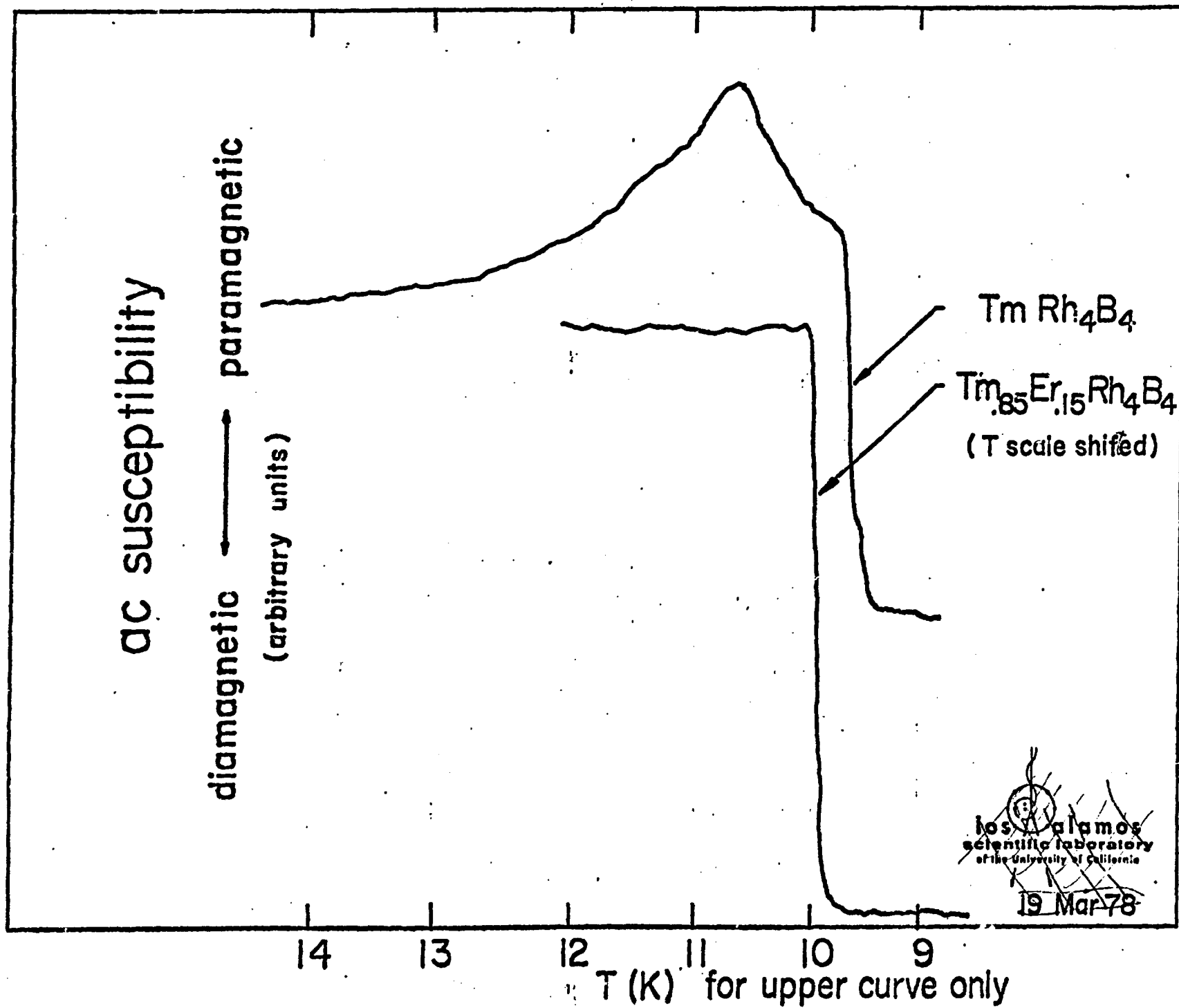
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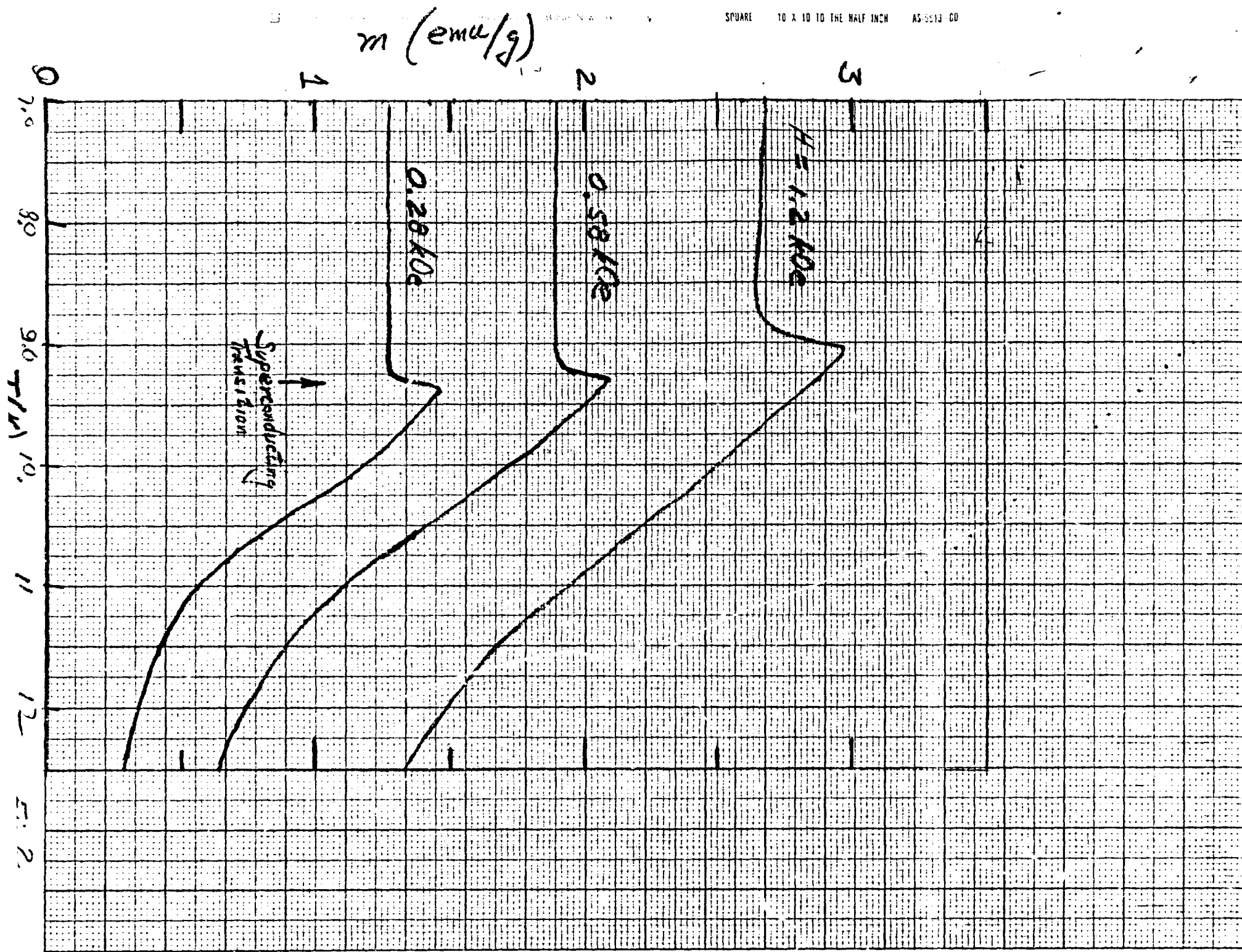
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FIGURE CAPTIONS

- Fig. 1. The ac susceptibility of TmRh_4B_4 and $\text{Er}_{.15}\text{Tm}_{.85}\text{Rh}_4\text{B}_4$.
- Fig. 2. The dc magnetization of TmRh_4B_4 as a function of temperature for various applied magnetic fields.
- Fig. 3. Heat capacity of TmRh_4B_4 with a LuRh_4B_4 background subtracted.

Fig. 1.





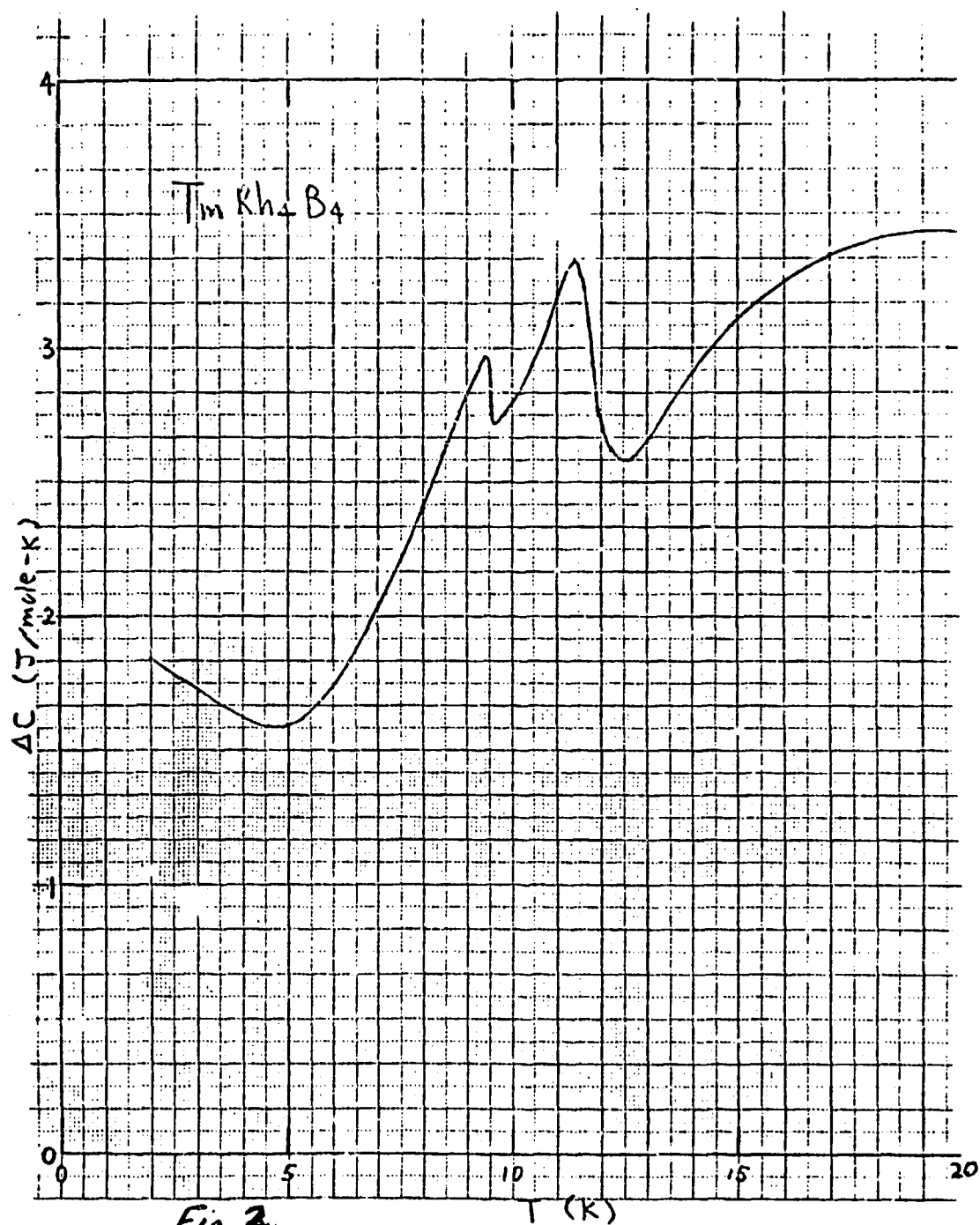


Fig. 3.